

DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

AD-A232 857

LECTE
R 14 1991

2b. DECLASSIFICATION

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
University of New Orleans6b. OFFICE SYMBOL
(If applicable)

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release;
distribution is unlimited.

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6c. ADDRESS (City, State, and ZIP Code)
Department of Chemistry
New Orleans, LA 701487b. ADDRESS (City, State, and ZIP Code)
Building 410
Bolling AFB, DC 20332-64488a. NAME OF FUNDING/SPONSORING
ORGANIZATION
AFOSR8b. OFFICE SYMBOL
(If applicable)
NC9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR-88-00688c. ADDRESS (City, State, and ZIP Code)
Building 410
Bolling AFB, DC 20332-6448

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.
61102FPROJECT
NO.
2303TASK
NO.
B3WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

(U) COMPUTATIONAL STUDIES OF ENERGETIC STRAINED MOLECULES: PROPERTIES AND SYNTHESSES
OF TETRAHEDRANE AND TRIPRISMANE SYSTEMS

12. PERSONAL AUTHOR(S)

Dr. Peter Politer, Department of Chemistry, University of New Orleans

13a. TYPE OF REPORT
Final Report13b. TIME COVERED
FROM 11/1/87 TO 10/31/9014. DATE OF REPORT (Year, Month, Day)
1990, 12, 1915. PAGE COUNT
14

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD GROUP SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

tetrahedrane; triprismane; azatetrahedranes; azatriprismanes;
nitro/amino derivatives; ab initio SCF calculations; strain;
bond strengths; electrostatic potentials; specific impulse.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

We have carried out ab initio self-consistent-field computational analyses and evaluations of nitro, amino, nitro/amino and nitro/methyl derivatives of the strained polyhedranes tetrahedrane, triprismane and their aza analogues. 3-21 G optimized geometries were computed, and used to calculate bond deviation indices (as measures of bond strain), bond orders (to determine relative bond strengths), molecular electrostatic potentials and surface average local ionization energies (as guides to reactive behavior), isodesmic reaction energies (as measures of total molecular strain) and relative stabilities of isomers. Specific impulse calculations showed that aza derivatives are favored over their hydrocarbon analogues as high performance monopropellants. From standpoints of stability, synthesis and high performance, we recommend that nitro and nitro-amino derivatives of azatetrahedranes and azatriprismanes be further explored as high energy density target systems.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

(202) 767-4566

22c. OFFICE SYMBOL

ALC

COMPLETED PROJECT SUMMARY

TITLE: Computational Studies of Energetic Strained Molecules: Properties and Syntheses of Tetrahedrane and Triprismane Systems

PRINCIPAL INVESTIGATOR: Dr. Peter Politzer
Department of Chemistry
University of New Orleans
New Orleans, Louisiana 70148

INCLUSIVE DATES: 1 November 1987 - 31 October 1990

CONTRACT/GRANT NUMBER: AFOSR-88-0068

TOTAL COST: \$310,381.

SENIOR RESEARCH PERSONNEL:	Dr. M. Edward Grice	Dr. Paul Redfern
	Dr. Michael Grodzicki	Dr. Jorge M. Seminario
	Dr. Jane S. Murray	

JUNIOR RESEARCH PERSONNEL:	Mr. Tore Brinck	Mrs. Monica Concha
	Ms. Anita Hamel	Mr. Dariush Habibollahzadeh
	Mrs. Pat Lane	Dr. Per Sjoberg

PUBLICATIONS:

"A Computational Determination of the Structures and Some Properties of Tetrahedrane, Prismane and Some of Their Aza Analogs", P. Politzer and J. M. Seminario, J. Phys. Chem., 93, 588 (1989).

"Relative Bond Strengths in Tetrahedrane, Prismane and Some of Their Aza Analogs", P. Politzer and J. M. Seminario, Struct. Chem., 1, 29 (1989).

"A Computational Analysis of the Structures, Bond Properties and Electrostatic Potentials of Some Nitrotetrahedranes and Nitroazetetrahedranes", P. Politzer and J. M. Seminario, J. Phys. Chem., 93, 4742 (1989).

"Analysis of Different Computational Treatments of Highly-Strained Molecules", J. M. Seminario and P. Politzer, Chem. Phys. Letters, 159, 27 (1989).

"Conformation-Dependent Effects of the Nitro Group Upon Some Strained Tertiary C-C Bonds", M. Grodzicki, J. M. Seminario and P. Politzer, J. Phys. Chem., 94, 624 (1990).

"Anomalous Energy Effects Associated with the Presence of Aza Nitrogens and Nitro Substituents in Some Strained Systems", J. S. Murray, J. M. Seminario, P. Lane and P. Politzer, J. Mol. Struct. (THEOCHEM), 207, 191 (1990).

"Average Local Ionization Energies Computed on the Surfaces of Some Strained Molecules", J. S. Murray, J. M. Seminario, P. Politzer and P. Sjoberg, Int. J. Quantum Chem., in press.

"A Computational Study of Relative Bond Strengths and Stabilities of a Series of Amine and Nitro Derivatives of Triprismane and Some Azatriprismanes", J. S. Murray, M. Concha, J. M. Seminario and P. Politzer, J. Phys. Chem., in press.

"A Computational Analysis of Relative Bond Strengths in Some Nitroazatriprismanes and Smaller Related Molecules", J. S. Murray, P. C. Redfern and P. Politzer, J. Phys. Chem., submitted for publication.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this project have been to carry out detailed computational analyses and evaluation of nitro, amino, nitro/amino and nitro/methyl derivatives of the strained polyhedranes tetrahedrane (I), triprismane (II), and their aza analogues. The key findings coming out of this three year study are listed below.



I



II

- (1) The introduction of aza nitrogens into the highly strained tetrahedrane and triprismane frameworks has a definite stabilizing effect. This is true for both the individual bonds and the molecule as a whole. Our calculated bond deviation indices and bond orders show that the C-C and C-N bonds become, overall, less strained and stronger as the number of aza nitrogens increases; concurrently the total molecular strain energy decreases. These findings suggest that strained aza molecules may represent promising frameworks for the design of energetic systems; the aza nitrogens may provide a means for mitigating excessive strain.
- (2) The substitution of aza nitrogens for CH groups results in a large increase in the heat of formation; thus the presence of the former is desirable from the standpoint of designing molecules with high specific impulse values.
- (3) There are negative electrostatic potentials associated with the C-C bonds in tetrahedrane and triprismane, indicating that these bonds can serve as initial sites for electrophilic attack. These potentials are greatly weakened or eliminated in the aza systems and are completely absent in the nitro derivatives, reflecting the electron-withdrawing power of the aza nitrogens and the nitro group.
- (4) In the azatetrahedranes and azatriprismanes, there are strong and extensive negative regions of electrostatic potential near the nitrogens, suggesting significant basicity. These become weaker as the number of nitrogens increases, and especially upon NO₂ substitution.
- (5) The rotation of nitro groups in the tetrahedranes is found to involve essentially no energy barrier. In the triprismanes, however, the NO₂ preferentially orients itself perpendicularly to the plane of the three-membered ring face, with a barrier to rotation of ~ 5 kcal/mole.
- (6) Polynitration of tetrahedranes and triprismanes increases overall molecular strain energy. The effects of mononitration are mixed, depending upon the number of aza nitrogens in the framework. Amino substituents consistently diminish molecular strain energy.
- (7) Nitro and amino groups have separate effects upon the endocyclic bond strengths of the tetrahedranes and triprismanes. We have found a consistent direction-specific bond weakening in one (and only one) of the C-C or C-N bonds adjacent to the site

For

I

d

ion

ion/

Availability Codes

Dist

Avail and/or
Special



A-1

of NH₂ substitution. The weakened C-X bond (where X = C or N) is invariably essentially coplanar with the C-NH₂ bond and the amine nitrogen "lone pair"; this tendency is a manifestation of the "anomeric effect". The situation involving the NO₂ group alone is more complicated, because it can strengthen some bonds and weaken others, depending upon its conformation. When the NO₂ and NH₂ are on adjacent carbons, these effects can reinforce under appropriate circumstances and cause significant bond weakening of the intervening C-C bond (often referred to as a "push-pull" mechanism).

- (8) Our computations have shown that tetrahedrane with adjacent NO₂ and NH₂ groups does not correspond to a stable structure; instead the system computationally rearranges to the cyclobutadiene isomer. A striking finding is that the presence of an aza nitrogen in the tetrahedrane framework prevents this rearrangement.
- (9) In the triprismane and azatriprismane frameworks, an absence of a "push-pull" mechanism for vicinal NO₂, NH₂ groups has also been found. Each of these substituents individually causes some significant bond-weakening, but they affect different bonds and thus do not reinforce.
- (10) From the standpoint of synthesis, our bond strength results indicate that the vicinal NO₂, NH₂ combination in azatetrahedrane, triprismane and its aza analogues should not be a problem (creating weak intervening bonds) in these systems, as it has been in the cubanes.
- (11) Our calculations of surface average local ionization energies suggest that the three-sided faces of tetrahedrane and triprismane have "σ-aromatic" character, as does cyclopropane, and are likely sites for electrophilic attack; these results are consistent with our electrostatic potential results.

RECOMMENDATIONS:

From standpoints of stability, synthesis and high performance, we recommend that nitro and nitro/amino derivatives of azatetrahedranes and azatriprismanes be further explored as high energy density target systems.

AFOSR PROJECT MANAGER: Lt. Col. Larry P. Davis, USAF

8 1 DEC 1990

FINAL REPORT

19 December 1990

Project Manager: Lt. Col. Larry P. Davis
Directorate of Chemical
and Atmospheric Sciences
Air Force Office of Scientific Research
Bolling Air Force Base, DC 20332-6448

Title of Project: COMPUTATIONAL STUDIES OF ENERGETIC
STRAINED MOLECULES: PROPERTIES AND
SYNTHESES OF TETRAHEDRANE AND
TRIPRISMANE SYSTEMS

Contract Number: AFOSR -88-0068

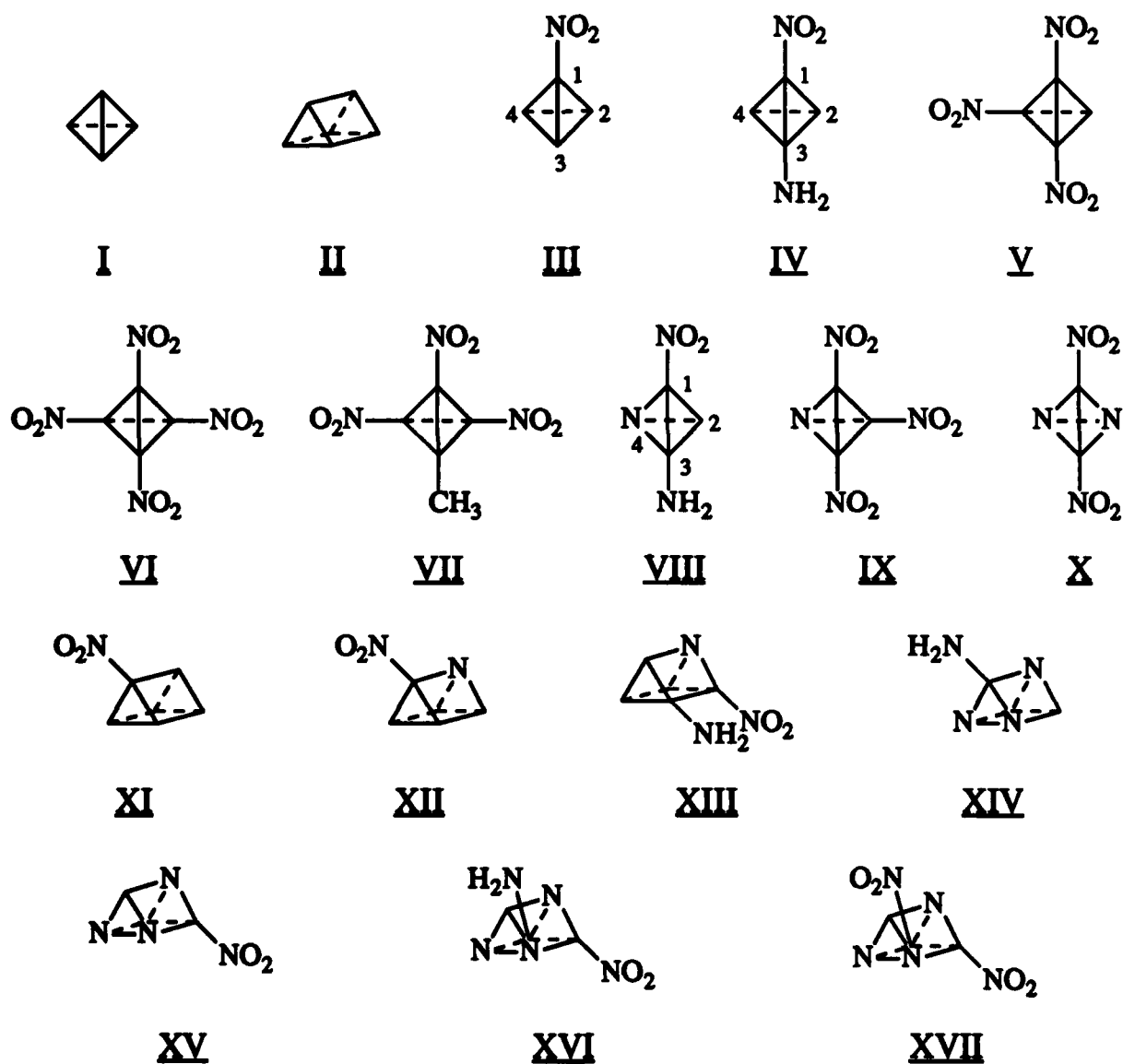
Inclusive Dates: 1 November 1987 - 31 October 1990.

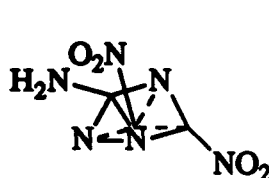
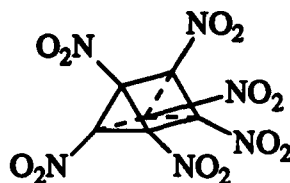
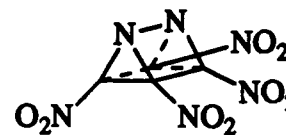
Principal Investigator: Dr. Peter Politzer
Department of Chemistry
University of New Orleans
New Orleans, LA 70148
Tel: (504) 286-6850

Approved for public release;
distribution unlimited.

I. Introduction

The objectives of this project have been to carry out detailed computational analyses and evaluation of certain strained polyhedrane molecules that are of potential importance as high energy density systems. The molecules studied have been nitro, amino, nitro/amino and nitro/methyl derivatives of tetrahedrane (I), triprismane (II) and their aza analogues, in which one or more C-H units have been replaced by nitrogens; many of these are shown below. Our main goal has been to identify and/or design systems that are particularly promising as high energy density materials.



XVIIIXIXXX

Our approach has been computational, using primarily the *ab initio* self-consistent-field molecular orbital GAUSSIAN programs [1-3] for calculating a variety of properties. Geometries have been optimized at the 3-21G level, and the resulting structures used to calculate bond deviation indices (as measures of bond strain), bond orders (to determine relative bond strengths), molecular electrostatic potentials and surface average local ionization energies (as guides to reactive behavior), isodesmic reaction energies (as measures of total molecular strain), and the relative stabilities of isomers. The results of these computations, many of which have been published or are in press [4-12], will be summarized in the next section.

II. Results and Discussion

A. Effects of Aza Nitrogens:

The introduction of aza nitrogens into the highly strained tetrahedrane and triprismane structures has a definite stabilizing effect. This is true both for the individual bonds and for the molecule as a whole. Our calculated bond deviation indices and bond orders show that the C-C and C-N bonds become, overall, less strained and stronger as the number of aza nitrogens increases [4,5];* concurrently, the total molecular strain energy decreases [9]. (The latter quantity is obtained by the isodesmic reaction procedure, and reflects all destabilizing factors arising from the mutual interactions of the different portions of the molecule [13].) We attribute the stabilizing effects of the aza nitrogens to σ -conjugation of their lone pairs [14], whereby the lone pair electronic density is delocalized to some degree through the σ -bond framework.

B. Effects of Nitro and Amino Groups:

1. Bond Strain and Total Molecular Strain Energy:

We find the presence of nitro substituents to have little effect upon the strain in individual bonds [6], a conclusion that we already reached in earlier work [15,16]. However the nitration of

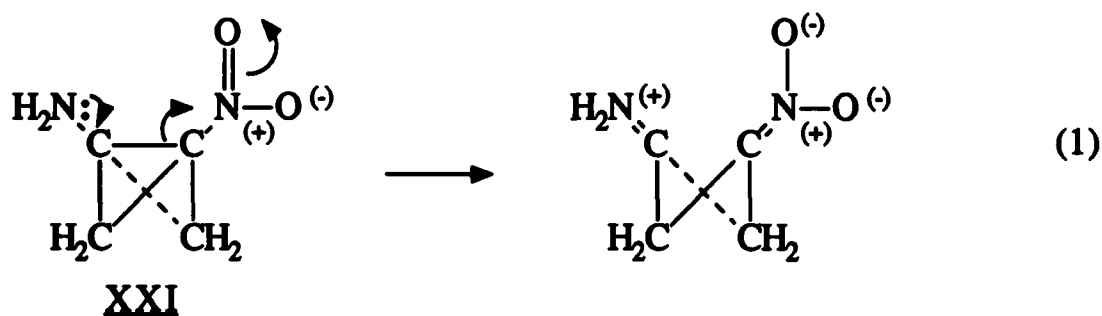
* The N-N bonds do not follow this trend, becoming slightly weaker instead.

systems containing highly strained tertiary carbons has mixed effects on the molecular strain energies [9,11]. In general the mononitration of such systems is slightly stabilizing, effecting a decrease in molecular strain energy, while polynitration leads to a marked increase. The substitution of NH_2 , on the other hand, is consistently stabilizing [11,18].

2. Bond Strengths:

We have found that an NO_2 substituent will somewhat strengthen some and weaken others of the strained bonds between tertiary carbons in these polyhedrane systems, depending upon its conformation relative to those bonds [6,8]. The C-C bond weakening produced by an NO_2 group was studied in particular detail in the case of nitrotetrahedrane, **III** [6,8]. When the O-N-O and N- C_1 - C_3 planes are perpendicular, as in the ground state, then the C_1 - C_3 and (to a lesser extent) the C_2 - C_4 bonds are weakened relative to unsubstituted tetrahedrane, while the C_1 - C_2 and C_1 - C_4 are strengthened. When the NO_2 group is rotated by 90° (which requires a 3-21G calculated energy of only 0.04 kcal/mole), these effects are reversed. By means of molecular orbital correlation analyses [8], we were able to show that these bond weakenings are due to interactions between a π -type orbital of the NO_2 group and C-C bonding orbitals of the tetrahedrane framework; for various orientations of the NO_2 , these interactions affect different C-C bonds.

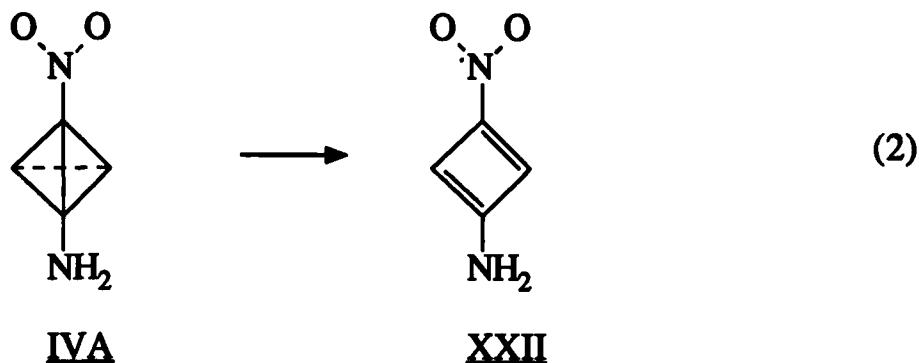
Some time ago, we showed that the strained bond between the two tertiary carbons in bicyclobutane would be very significantly weakened if an NO_2 and an NH_2 substituent were present simultaneously on these carbons, **XXI** [15]. This weakening was interpreted in terms of a contribution from the mechanism that is shown, for the case of total disruption, in eq. (1):



The particular importance of this finding comes about because (a) mixed NO_2 - NH_2 derivatives may be desirable energetic materials in their own right, and (b) they are precursors in some preparative routes to the synthesis of polynitro systems.

In the course of a discussion with Lt. Col. Larry P. Davis (AFOSR) in January 1989, it was decided that in view of the C-C weakening that NO_2 alone can produce in tetrahedrane, it would be highly desirable to determine the consequences of NO_2 and NH_2 being substituted simultaneously on tetrahedrane, as in **IV**. We found these to be rather dramatic [8]: when the

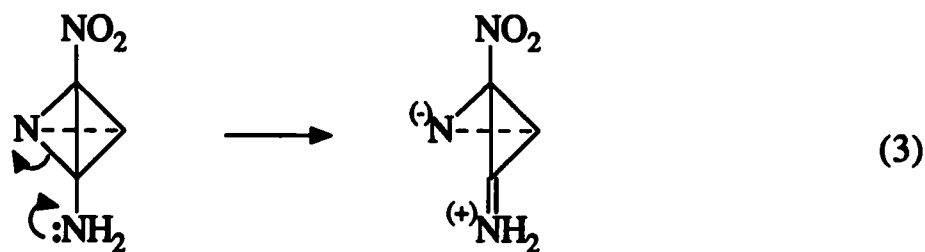
O-N-O and N-C₁-C₃ planes are initially perpendicular (**IVA**), the molecule actually undergoes a rearrangement to 1-nitro-3-aminocyclobutadiene, **XXII**:



Thus, in the very highly strained tetrahedrane framework, the amine group evidently reinforces the weakening of the C-C bond to the extent that the mechanism shown in eq. (1) is able to completely break it.

In contrast, no such striking effects are observed when the O-N-O and N-C₁-C₃ planes in **IV** coincide. The tetrahedrane structure is retained, and there occur only minor strengthenings and weakenings of the C-C bonds, as described above for nitrotetrahedrane..

It is highly significant that when an aza nitrogen is incorporated into the tetrahedrane framework (structure **VIII**), no rearrangement of the type shown in eq. (2) occurs even if the O-N-O and N-C₁-C₃ planes are perpendicular [8]. Regardless of the initial NO₂ conformation, the system assumes the same final structure, which has the molecular framework of tetrahedrane and an 18° dihedral angle between the O-N-O and N-C₁-C₃ planes. The calculated geometry indicates that the mechanism depicted in eq. (3) may have some influence:

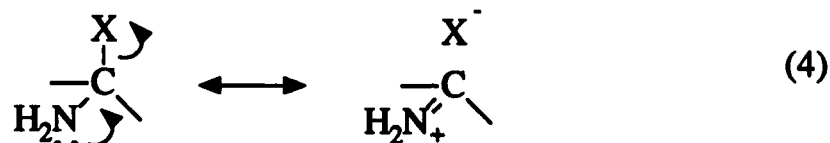


The tendency for some shifting of charge in accordance with eq. (3) may be providing an alternative to that shown in eq. (1), which would explain why the presence of the aza nitrogen prevents the rearrangement shown in eq. (2).

Eq. (3) does indicate that a weakening of the C₃-N₄ bond is to be anticipated in **VIII**, and this is confirmed by our calculated bond orders. However this weakening is not found to be sufficient to disrupt the molecular framework, as occurred in **IVA**. This suggests that mixed

NO₂-NH₂ derivatives may be acceptable for azatetrahedrane systems, even though not for tetrahedrane itself.

In some recent related computational analyses, we have found that the "push-pull" mechanism depicted by eq. (1) is actually the consequence of two separate effects, associated with the NH₂ and NO₂ groups individually, which can reinforce each other under appropriate circumstances [11,17,18]. In studies of some amino- and aminonitrocubanes, azacubanes, triprismanes and azatriprismanes [11,17,18], we have found a consistent direction-specific bond weakening in one (and only one) of the C-C or C-N bonds adjacent to the site of NH₂ substitution. The weakened C-X bond (where X=C or N) is invariably essentially coplanar with the C-NH₂ bond and the position of the most negative electrostatic potential [$V_{\min}(\text{N})$] associated with the amine nitrogen lone pair [11,17,18]. The tendency for a coplanar alignment of the lone pair and a C-X bond is a manifestation of the anomeric effect [14], and reflects the possibility of the delocalization of the lone pair as shown in eq. (4). (A specific example of this is given by eq. (3).)



This delocalization, which is seen to weaken the C-X bond, can occur most effectively when the bond is coplanar with the lone pair. The anomeric effect is most commonly invoked for molecules in which X is an electronegative atom, e.g. O, N or F [14]; however we have also observed this tendency (although it is not so strong) when X=C [11,17,18].

The situation involving the NO₂ group alone is more complicated, because it can strengthen some bonds and weaken others, depending on its conformation [6,8,18], as we have already discussed. The patterns that have been described for NH₂ and NO₂ substituents individually are equally applicable when they are simultaneously substituted on strained tertiary carbons within the same molecule [8,11,15,18]. If the substituted carbons are adjacent to one another, reinforcement can occur under appropriate circumstances [8,15,18].

A striking finding that has come out of our recent study of nitro and amino derivatives of triprismane and some azatriprismanes [11] is that such reinforcement does not occur in the triprismane framework when NO₂ and NH₂ are on adjacent carbons; indeed they do not even affect the same C-C (or C-N) bond. This is an important difference between the triprismane systems and other strained cage-like molecules that we have studied. From the standpoint of synthesis, our results indicate that the vicinal NH₂, NO₂ combination should not be a problem in the triprismane systems, as it has been in the cubanes [19,20]. On the other hand, the NH₂ can produce

considerable bond weakening [11,17,18]. It may be that the overall stabilization imparted by the amino group [11,17,18] compensates, at least partially, for its effects on certain bonds.

An interesting observation that has come out of our work on caged polyhedranes is that when there are several isomeric structures, the most energetically stable is often the one that has the most pronounced weakening of individual bonds [8,11,17,18]. This presumably reflects the overall stabilization that accompanies the delocalization of electronic charge, even when the delocalization leads to the weakening of certain bonds.

Our results in general have revealed unexpected complexities in the role of the nitro group and its intramolecular interactions in strained cage-like systems [6,8,11,12,18]. In nitrotetrahedrane and nitrocubane and azacubanes there are very low barriers to rotation of the nitro group [6,8,18]. In triprismane and azatriprismane, however, there is a definite preference for the NO_2 to orient itself perpendicular to the three-sided face of the cage [11,12]; this is consistent with findings for nitrocyclopropane and azacyclopropane [12].

C. Electrostatic Potentials:

We have found negative electrostatic potentials to be associated with the C-C bonds in tetrahedrane and triprismane [4], indicating that these bonds can serve as initial sites for electrophilic attack. (We have shown such negative bond potentials to be characteristic of strained hydrocarbons, and fully consistent with their experimentally-observed reactive behavior [15,16,21-24].) These potentials are greatly weakened or eliminated in the azatetrahedranes and azatriprismanes [4], implying diminished susceptibility toward electrophiles, and are completely absent in the nitro derivatives [6], reflecting the electron-withdrawing power of the aza nitrogens and the nitro group.

In the azatetrahedranes (VIII - X) and azatriprismanes, there are strong and extensive negative regions near the nitrogens, indicative of significant basicity [4]. These become weaker (less basic) as the number of nitrogens increases, and especially upon NO_2 substitution [4,6].

D. Specific Impulse Calculations:

The specific impulse is a quantitative measure of the thrust developed by an energetic material during its combustion. Because of the importance of this property as a means of evaluating propellants, we have now calculated it for approximately seventy different molecules, of a wide variety of types. We have used both our own program and also one obtained from the Naval Weapons Center (China Lake, CA); we have confirmed that the results obtained by these two approaches give relative values that are in very good agreement with each other. As a

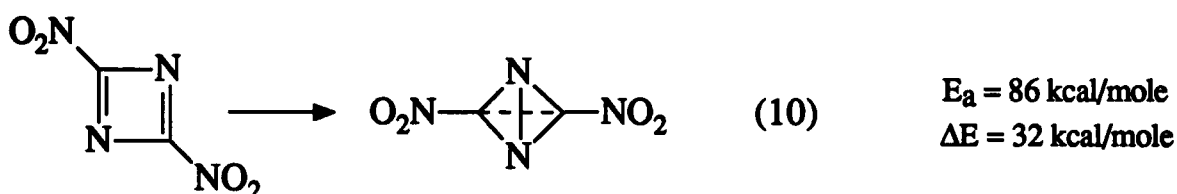
consequence of having calculated the specific impulses of so many molecules, we have developed a good practical understanding of the molecular structural features that help to produce high values. It is desirable to try to satisfy two key criteria: (a) combustion should lead to light gaseous products, so as to maximize the number of moles of gases produced per unit weight of propellant; and (b) the compound should have a large positive heat of formation (on a weight basis), since this results in a high combustion temperature. The presence of strain and aza nitrogens favors a high heat of formation (which is defined relative to the very stable N_2), while the inclusion of some hydrogens (and fluorines) results in light gases (H_2O and HF) being formed as combustion products [25].

E. Energetics of Conversions of Benzene and Azabenzenes to Triprismane and Azatriprismanes:

It is known that certain benzene and monoazabenzene (pyridine) derivatives can be converted photolytically to the corresponding isomeric triprismane and azatriprismane systems [13,26-28]. Such processes could conceivably be the basis for preparing polynitrotriprismanes and polynitroazatriprismanes, either by one-step isomerizations of the corresponding nitroaromatics or by isomerizations of other aromatic systems followed by conversion to nitro derivatives.

It is anticipated that these reactions would be endothermic, and therefore the transition states are expected to resemble the products (Hammond's Postulate [29]). In view of our finding that the presence of aza nitrogens stabilizes strained molecules [9], it seemed worthwhile investigating the possibility that this may extend to some of the transition states as well, and would facilitate conversions to azatriprismanes and azatetrahedranes. We have accordingly computed the activation barriers, E_a , and total energy changes, ΔE , for reactions (5) - (10) [25]. All geometries were optimized with the 3-21G basis set; these were then used to compute the energies with a local density functional approach that includes correlation energy [30].





The results are given above. The transition states in (5) - (7) can be regarded as essentially boat-type structures. In these limited examples, the effects of the aza nitrogens are seen to be mixed. The data do show, however, that the isomerizations described by eqs. (7) and (9) are favored kinetically over the analogous benzene \rightarrow triprismane and cyclobutadiene \rightarrow tetrahedrane conversions. The calculated activation barriers for the processes given in eqs. (7) - (10) are in the general neighborhood of the radiation energy used for some of the known photolytic conversions [26-28], e.g. the commonly used wavelength 254 nm translates to about 100 kcal/mole.

F. Average Local Ionization Energies:

We have computed the average local ionization energy $\bar{I}(\mathbf{r})$ on surfaces encompassing a variety of strained molecules, including tetrahedrane, triprismane, diazatetrahedrane and nitrotetrahedrane [10]. $\bar{I}(\mathbf{r})$ is rigorously defined within the framework of SCF-MO theory and can be interpreted as the average energy needed to ionize an electron at any point in the space of a molecule. Thus, the positions of the smallest $\bar{I}(\mathbf{r})$ values ($\bar{I}_{S,\min}$) on the surfaces of molecules are the sites expected to be the most reactive to electrophiles. We find $\bar{I}_{S,\min}$ near the C-C bond midpoints of saturated three-membered, but not four-membered, hydrocarbon rings. These $\bar{I}_{S,\min}$ are interpreted as reflecting the " σ -aromatic" character of the former [10].

III. SUMMARY

The key findings coming out of this three year project are listed below.

- (1) The introduction of aza nitrogens into the highly strained tetrahedrane and triprismane frameworks has a definite stabilizing effect. This is true for both the individual bonds and the molecule as a whole. Our calculated bond deviation indices and bond orders show that the C-C and C-N bonds become, overall, less strained and stronger as the number of aza nitrogens increases; concurrently the total molecular strain energy decreases. These findings suggest that strained aza molecules may represent promising frameworks for the design of energetic systems; the aza nitrogens may provide a means for mitigating excessive strain.
- (2) The substitution of aza nitrogens for CH groups results in a large increase in the heat of formation; thus the presence of the former is desirable from the standpoint of designing molecules with high specific impulse values.
- (3) There are negative electrostatic potentials associated with the C-C bonds in tetrahedrane and triprismane, indicating that these bonds can serve as initial sites for electrophilic attack. These potentials are greatly weakened or eliminated in the aza systems and are completely absent in the nitro derivatives, reflecting the electron-withdrawing power of the aza nitrogens and the nitro group.
- (4) In the azatetrahedranes and azatriprismanes, there are strong and extensive negative regions of electrostatic potential near the nitrogens, suggesting significant basicity. These become weaker as the number of nitrogens increases, and especially upon NO₂ substitution.
- (5) The rotation of nitro groups in the tetrahedranes is found to involve essentially no energy barrier. In the triprismanes, however, the NO₂ preferentially orients itself perpendicularly to the plane of the three-membered ring face, with a barrier to rotation of ~ 5 kcal/mole.
- (6) Polynitration of tetrahedranes and triprismanes increases overall molecular strain energy. The effects of mononitration are mixed, depending upon the number of aza nitrogens in the framework. Amino substituents consistently diminish molecular strain energy.
- (7) Nitro and amino groups have separate effects upon the endocyclic bond strengths of the tetrahedranes and triprismanes. We have found a consistent direction-specific bond weakening in one (and only one) of the C-C or C-N bonds adjacent to the site of NH₂ substitution. The weakened C-X bond (where X = C or N) is invariably essentially coplanar with the C-NH₂ bond and the amine nitrogen "lone pair"; this tendency is a manifestation of the "anomeric effect". The situation involving the NO₂ group alone is more complicated, because it can strengthen some bonds and weaken others, depending upon its conformation. When the NO₂ and NH₂ are on adjacent carbons, these effects can reinforce under

appropriate circumstances and cause significant bond weakening of the intervening C-C bond (often referred to as a "push-pull" mechanism).

- (8) Our computations have shown that tetrahedrane with adjacent NO₂ and NH₂ groups does not correspond to a stable structure; instead the system computationally rearranges to the cyclobutadiene isomer. A striking finding is that the presence of an aza nitrogen in the tetrahedrane framework prevents this rearrangement.
- (9) In the triprismane and azatriprismane frameworks, an absence of a "push-pull" mechanism for vicinal NO₂, NH₂ groups has also been found. Each of these substituents individually causes some significant bond-weakening, but they affect different bonds and thus do not reinforce.
- (10) From the standpoint of synthesis, our bond strength results indicate that the vicinal NO₂, NH₂ combination in azatetrahedrane, triprismane and its aza analogues should not be a problem (creating weak intervening bonds) in these systems, as it has been in the cubanes.
- (11) Our calculations of surface average local ionization energies suggest that the three-sided faces of tetrahedrane and triprismane have "σ-aromatic" character, as does cyclopropane, and are likely sites for electrophilic attack; these results are consistent with our electrostatic potential results.

From standpoints of stability, synthesis and high performance, we recommend that nitro and nitro/amino derivatives of azatetrahedranes and azatriprismanes be further explored as high energy density target systems.

IV. References

1. GAUSSIAN 82: J. S. Binkley, M. J. Frisch, D. J. DeFrees, R. Krishnan, R. A. Whiteside, H. B. Schlegel, E. M. Fluder, and J. A. Pople GAUSSIAN 82, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 15213.
2. GAUSSIAN 86: M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
3. GAUSSIAN 88: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol and J. A. Pople, GAUSSIAN 88, Gaussian Inc., Pittsburgh, PA, 1988.
4. P. Politzer and J. M. Seminario, J. Phys. Chem., 93, 588 (1989).
5. P. Politzer and J. M. Seminario, Struct. Chem., 1, 29 (1989).
6. P. Politzer and J. M. Seminario, J. Phys. Chem., 93, 4742 (1989).
7. J. M. Seminario and P. Politzer, Chem. Phys. Letters, 159, 27 (1989).
8. M. Grodzicki, J. M. Seminario and P. Politzer, J. Phys. Chem., 94, 624 (1990).
9. J. S. Murray, J. M. Seminario, P. Lane and P. Politzer, J. Mol. Struct. (THEOCHEM), 207, 191 (1990).
10. J. S. Murray, J. M. Seminario, P. Politzer and P. Sjöberg, Int. J. Quantum Chem., in press.

11. J. S. Murray, M. Concha, J. M. Seminario and P. Politzer, *J. Phys. Chem.*, in press.
12. J. S. Murray, P. C. Redfern and P. Politzer, *J. Phys. Chem.*, submitted.
13. A. Greenberg and J. F. Liebman, *Strained Organic Molecules*; Academic Press: New York, 1978.
14. M. J. S. Dewar, *J. Am. Chem. Soc.* **106**, 669 (1984).
15. P. Politzer, G. P. Kirschenheuter and J. Alster, *J. Amer. Chem. Soc.*, **109**, 1033 (1987).
16. P. Politzer and J. S. Murray, in *Molecular Structure and Energetics*, Vol 7, J. F. Liebman and A. Greenberg, eds., VCH Publishers, New York, 1988, Ch. 1.
17. J. S. Murray, J. M. Seminario and P. Politzer, *Structural Chem.*, submitted.
18. J. S. Murray, J. M. Seminario and P. Politzer, *Structural Chem.*, in press.
19. A. P. Marchand, *Tetrahedron* **44**, 2377 (1988).
20. G. W. Griffin and A. P. Marchand, *Chem. Rev.* **89**, 997 (1989).
21. P. Politzer, L. N. Domelsmith, P. Sjöberg and J. Alster, *Chem. Phys. Lett.*, **92**, 366 (1982).
22. P. Politzer, L. N. Domelsmith and L. Abrahamsen, *J. Phys. Chem.*, **88**, 1752 (1984).
23. P. Politzer, K. Jayasuriya and B. A. Zilles, *J. Amer. Chem. Soc.*, **107**, 121 (1985).
24. P. Politzer and K. Jayasuriya, in Special Issue of THEOCHEM (Journal of Molecular Structure) in Honor of Professor Robert S. Mulliken, **135**, 245 (1986).
25. P. Politzer, J. M. Seminario, J. S. Murray and M. Grodzicki, Proc. High Energy Density Materials Contractors Conference, Long Beach, CA, 25 - 28 February, 1990.
26. H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders and P. Valange, *Angew. Chem., Int. Ed. Engl.* **3**, 755 (1964).
27. K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.* **87**, 4004 (1965).
28. A. R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York, 1985.
29. G. S. Hammond, *J. Am. Chem. Soc.* **77**, 334 (1955).
30. DMol, published by BIOSYM Technologies, Inc., San Diego, CA.

IV. Research Publications Resulting From This Project:

Articles in print:

- (1) "A Computational Determination of the Structures and Some Properties of Tetrahedrane, Prismane and Some of Their Aza Analogs"
P. Politzer and J. M. Seminario, *J. Phys. Chem.*, **93**, 588 (1989).
- (2) "Relative Bond Strengths in Tetrahedrane, Prismane and Some of Their Aza Analogs"
P. Politzer and J. M. Seminario, *Struct. Chem.*, **1**, 29 (1989).
- (3) "A Computational Analysis of the Structures, Bond Properties and Electrostatic Potentials of Some Nitrotetrahedranes and Nitroazetetrahedranes"
P. Politzer and J. M. Seminario, *J. Phys. Chem.*, **93**, 4742 (1989).
- (4) "Analysis of Different Computational Treatments of Highly-Strained Molecules"
J. M. Seminario and P. Politzer, *Chem. Phys. Letters*, **159**, 27 (1989).
- (5) "Conformation-Dependent Effects of the Nitro Group Upon Some Strained Tertiary C-C Bonds"
M. Grodzicki, J. M. Seminario and P. Politzer, *J. Phys. Chem.*, **94**, 624 (1990).
- (6) "Anomalous Energy Effects Associated with the Presence of Aza Nitrogens and Nitro Substituents in Some Strained Systems"
J. S. Murray, J. M. Seminario, P. Lane and P. Politzer, *J. Mol. Struct. (THEOCHEM)*, **207**, 191 (1990).

Articles accepted for publication and in press:

- (7) "Average Local Ionization Energies Computed on the Surfaces of Some Strained Molecules"
J. S. Murray, J. M. Seminario, P. Politzer and P. Sjoberg,
Int. J. Quantum Chem., in press.
- (8) "A Computational Study of Relative Bond Strengths and Stabilities of a Series of Amine and Nitro Derivatives of Triprismane and Some Azatriprismanes"
J. S. Murray, M. Concha, J. M. Seminario and P. Politzer, J. Phys. Chem., in press.

Article submitted for publication:

- (9) "A Computational Analysis of Relative Bond Strengths in Some Nitroazatriprismanes and Smaller Related Molecules"
J. S. Murray, P. C. Redfern and P. Politzer, J. Phys. Chem., submitted.

VI. Personnel Associated with this Project

Dr. Peter Politzer	Principal Investigator
Mr. Tore Brinck	Graduate Research Assistant
Mrs. Monica Concha	Research Assistant
Dr. M. Edward Grice	Research Associate
Dr. Michael Grodzicki	Research Associate
Mr. Dariush Habibollahzadeh	Graduate Research Assistant
Ms. Anita Hamel	Research Associate
Mrs. Pat Lane	Research Associate
Dr. Jane S. Murray	Research Associate
Dr. Paul Redfern	Research Associate
Dr. Jorge M. Seminario	Research Associate
Dr. Per Sjoberg	Graduate Research Assistant

VII. Professional Interactions Related To This Project

- (1) Presentation at AFOSR High Energy Density Materials Contractors Conference, Newport Beach, CA, February 29 - March 2, 1988.
Title: "Computational Studies of the Properties of Tetrahedrane, Triprismane and Their Aza Analogs," by P. Politzer and J. M. Seminario; presented by P. Politzer.
- (2) Presentation of AFOSR High Energy Density Materials Contractors Conference, New Orleans, LA, March 12 - 15, 1989.
Title: "Computational Studies of Tetrahedrane, Some Azatetrahedranes, and Their Nitro Derivatives," by P. Politzer and J. M. Seminario; presented by P. Politzer.
- (3) Discussions with Dr. David S. Ross (SRI International) regarding possible conversions of polynitroaromatic systems to the isomeric polynitrotriprismanes. These would be single-step processes, induced by high pressure and/or photolysis.

- (4) Presentation at AFOSR High Energy Density Materials Contractors Conference, Long Beach, CA, February 25 - 28, 1990.
Title: "Computational Analyses of Some Nitrotetrahedranes, Nitrotriprismanes and Their Aza Analogues," by P. Politzer, J. M. Seminario, J. S. Murray and M. Grodzicki; presented by P. Politzer.
- (5) Participated in AFOSR Computational Chemistry Conference, Albuquerque, NM, May 1990.
- (6) Presentation at the Ninth Annual Working Group Institute on Synthesis of High Energy Density Materials, Monticello, NY, June 4 - 7, 1990.
Title: "Computational Studies of the Properties of Strained Aza Systems," by P. Politzer.